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Modes of Attachment of Pyridine to Gold Surfaces

by

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The adsorption of pyridine onto both polycrystalline and single crystal gold electrode surfaces has been investigated using three electrochemical techniques: cyclic voltammetry, differential capacity and chronocoulometry. The surface concentration of pyridine, the Gibbs energy of adsorption, the electrosorption valency and the orientation of the pyridine molecules on the gold electrode surfaces, have been measured. All of these parameters were found to be sensitive to the structure of the gold electrode surface...

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Modes of Attachment of Pyridine to Gold Surfaces

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Introduction

This work is part of a project which is devoted to studying the influence of crystallographic orientation of gold electrodes on the adsorption of pyridine from aqueous electrolyte solutions. We are trying to determine how the orientation of the adsorbed pyridine molecule and the energetics of its adsorption are governed by the geometry and density of coordination centres present at the electrode surface. Data are presented for the adsorption of pyridine onto polycrystalline gold, Au(100), Au(110) and Au(111).

Previously, Hamelin and Valette (1) investigated pyridine adsorption on gold single crystal electrode surfaces using differential capacity. These works have provided qualitative information on pyridine adsorption and have shown that there is a strong influence of the surface morphology on the adsorption process. We have extended this work by obtaining quantitative data using an electrochemical technique known as chronocoulometry. Adsorption isotherms, Gibbs energies of adsorption, electrosorption valencies and the orientation of the pyridine molecules on the various gold electrode surfaces have been determined and will be discussed.

Results and Discussion

Pyridine adsorption studies on Au(100) have shown, that, over the potential region -0.8 V to +0.6 V (SCE) three orientations of the pyridine molecules are possible. At a positively charged surface, the pyridine molecules assume a vertical orientation with the nitrogen atom facing the gold surface. A limiting surface concentration of 6×10^{-10} mol cm^{-2} was determined for this orientation. At a negatively charged surface and at low surface concentrations ($\Gamma < 1 \times 10^{-10}$ mol cm^{-2}) the pyridine molecules adsorb flat with the aromatic ring oriented parallel to the surface. At intermediate surface coverages (3×10^{-10} mol cm$^{-2} > \Gamma > 1 \times 10^{-10}$ mol cm^{-2}) and for potentials close to zero charge, a third orientation, presumably intermediate between the flat and the vertical orientations, was observed. Evidence for these latter two orientations has come our film pressure data as well as from an analysis of the potential drop across the inner layer region of the double layer. Reorientation between the intermediate orientation and the vertical orientation is the result of a phase transition.

For pyridine adsorbed onto a Au(110) single crystal electrode surface the surface concentration-potential curves also displayed a region characterized by a well defined plateau. The value of the limiting surface concentration was 6.14×10^{-10} mol cm^{-2} indicating that the pyridine molecules were oriented on the Au(110) surface in the vertical position. From the shift of the potential of zero charge we were able to infer that the nitrogen atom of the pyridine molecule must be facing the gold surface.

Pyridine adsorption onto Au(111) is a very interesting case. Here we see clear evidence for the flat orientation which occurs on a negatively charged electrode surface. The flat orientation is characterized by a limiting surface concentration of 1.4×10^{-10} mol cm^{-2}. Close to the potential of zero charge the pyridine molecules undergo a reorientation and assume the vertical position. This reorientation, like on Au(100), is the consequence of a phase transition. The value of the limiting surface concentration corresponding to the vertical orientation was found to be 6.73×10^{-10} mol cm^{-2}.

For pyridine adsorbed onto a polycrystalline gold electrode surface we will show that pyridine adsorption can best be described in terms of the adsorption onto different single crystal microfacets which make up the polycrystalline surface.

In general, the Gibbs energy of adsorption for all the gold electrodes discussed above has been found to reach maximum values as high as -35 to -38 KJ mol^{-1}. These are quite large values and suggest that the interactions between the various gold surfaces and the pyridine molecules are quite strong. From the electrosorption valencies, whose absolute values are large, one can infer that the pyridine molecules are chemisorbed.

Conclusions

The above results indicate that the orientation and energetics of pyridine adsorption onto gold electrode surfaces is influenced greatly by the crystallographic orientation of the gold surface.

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